
Novel Structured Metal Bipolar Plates for Low-Cost Manufacturing

Conghua “CH” Wang
TreadStone Technologies, Inc.
201 Washington Road
Princeton, NJ 08543
Phone: 609-734-3071
Email: cwang@TreadStone-Technologies.com

DOE Manager: Bahman Habibzadeh
Phone: 202-287-1657
Email: Bahman.Habibzadeh@ee.doc.gov

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Overall Objectives

- Develop the physical vapor deposition (PVD) process for the doped titanium oxide (TiO_x) coating.
- Characterize the doped TiO_x-coated metal plates, including the chemical composition and thickness of the doped TiO_x surface layer, the electrical contact resistance, and the corrosion resistance of the coating for proton exchange membrane (PEM) fuel cell applications.
- Evaluate the coating on low-cost stainless steel (SS) and post-coating stamping.
- Analyze the manufacturing cost of the technology.

Fiscal Year (FY) 2019 Objectives

- Develop the PVD process for the doped TiO_x coating.

- Design sputtering target to minimize the coating surface layer composition segregation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (A) Durability (improve the durability of bipolar plates in fuel cell operation conditions)
- (B) Cost (reduce the cost of the bipolar plate production)
- (C) Performance (improve the performance of the bipolar plates).

Technical Targets

The technical objective of the project is to further develop the manufacturing process of the doped TiO_x coating for PEM fuel cell applications that meet the following targets.

- Low electrical contact resistance with gas diffusion layer (<5 mΩ.cm²).
- Low corrosion resistance: < 1 μA/cm².
- Low cost: \$3/kW by 2020.
- Capable of roll-to-roll coating and post-coating stamping.

FY 2019 Accomplishments

- Reduced the deposition time of the TiO_x coating for low-cost manufacturing.
- Optimized the target composition to eliminate the coating surface layer composition segregation.
- Filed three provisional patent applications.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

Introduction

The components of the transportation fuel cell system and stack play an important role in the cost reduction and performance improvement of the fuel cell system. The metal bipolar plate is an important component in a fuel cell stack. For example, the automobile industry has confirmed that metal bipolar plates are essential to ensure rapid start of fuel cell vehicles in cold weather (-40°C). The metal plate cost is a significant part of the fuel cell stack cost. Figure 1 shows results of the PEM stack cost analysis recently (December 2015) conducted by our team partner Strategic Analysis, Inc. It shows that bipolar plates account for 14%–27% of the overall stack cost (1,000–500,000 stacks/year using 2015 technology) [1]. Therefore, any reduction in plate costs will have significant impact on the overall stack cost.

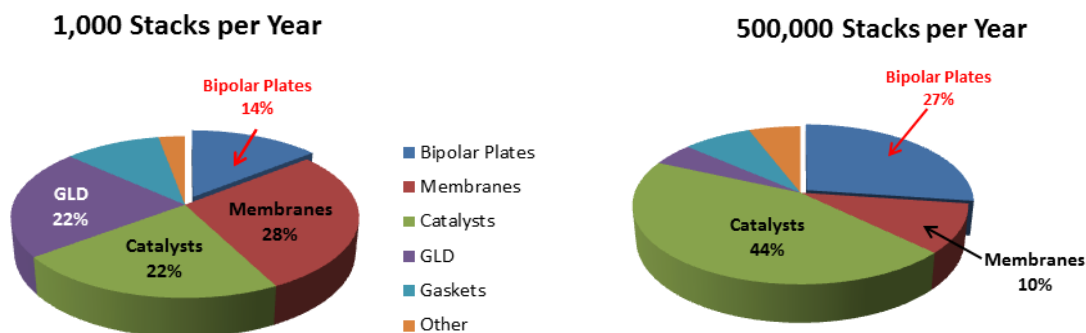


Figure 1. Cost breakdown of PEM fuel cell stacks [1]

Approach

The technical approach of this project is to develop a precious-metal-free coating technology for PEM fuel cell applications. The schematic drawing of the technology is shown in Figure 2. The SS foil substrate surface is covered with a thin ($\sim 100\text{-nm}$ thick) titanium alloy sublayer and an ultrathin (several nanometers) electrically conductive doped TiO_x surface layer. This surface oxide layer is grown on the titanium alloy sublayer surface. The titanium alloy contains the alloy element that is the dopant in the doped TiO_x .

TreadStone's approach overcomes the key technical barriers of using doped titanium oxide semiconductive material [2,3] as the coating material, which are: (1) the thickness control of the oxide coating layer, and (2) the adhesion of the oxide layer with the metal substrate. The technology utilizes the inherent characteristics of titanium alloys to overcome these barriers and makes it reliable at large-volume fabrication and low cost.

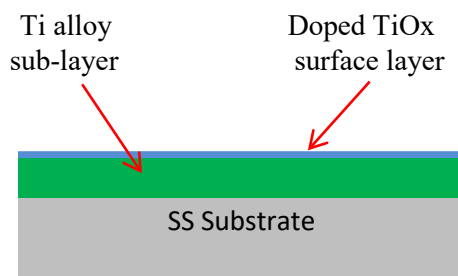


Figure 2. Schematic drawing of TreadStone's doped TiO_x coating on SS foil

Results

The cathodic arc deposition experiment was carried out with pure Ti targets with a Metco cathodic arc evaporation (CAE) system. At normal deposition conditions, the CAE process used for the surface coating deposition needs more than 1 hour to finish the coating process, which is not acceptable for high-volume production. In this period of the project, we have developed the modified deposition process that can significantly reduce the processing time. It was found that the longer deposition time process will deposit more particles in the coating layer that forms stand-outs on the coating surface. The electrical interface contact

resistance (ICR) of the CAE Ti-coated SS with surface stand-outs was measured using Teflon-free AvCarb MGL 190 carbon paper. To mimic the end of life plate electrical contact resistance, a ~15 nm thick titanium oxide layer was formed on the plate surface by thermal oxidization of the coated plate in air. The contact resistance of the plate with 15 nm thick surface oxide layer is shown in Figure 3. The ICR of the SS foils treated with the 5-, 10-, and 20-minute process meets DOE's performance target ($<10 \text{ m}\Omega\cdot\text{cm}^2$). The longer deposition time will lead to slightly lower ICR because more surface stand-outs are formed on the surface. Nevertheless, the 5-minute process is sufficient to meet the performance target. This rapid process is suitable for high-volume production of fuel cell bipolar plates.

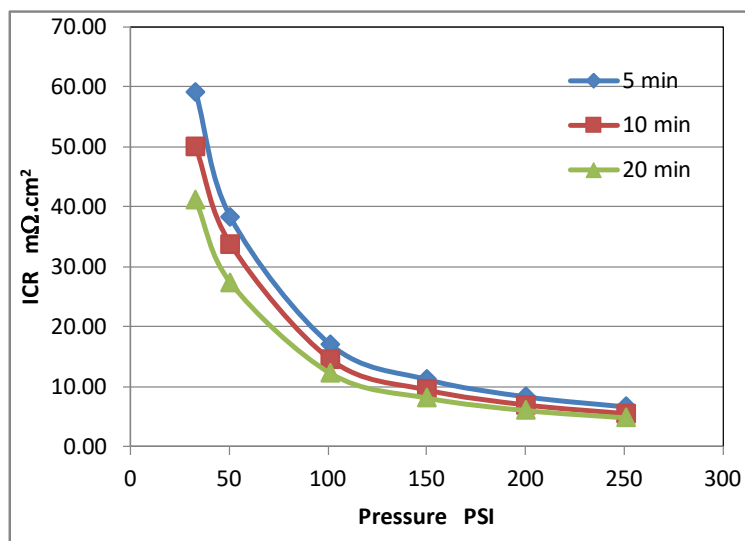


Figure 3. Comparison of ICR of doped TiOx-coated SS foil using PVD process with different deposition times

It was reported previously that the ICR of SS plates of regular “flat” titanium coated surface with ~15 nm thick surface oxide layer was several hundred $\text{m}\Omega\cdot\text{cm}^2$ at 200 psi compression pressure. It appears that the surface stand-outs in the coating structure can effectively reduce ICR of metal plates [4].

In FY 2019, we have tested different sputtering conditions to maintain Nb in the coating surface layer. The hypothesis is that composition segregation of the coating surface layer is caused by the slower velocity of Ti vapor than that of Nb, after sputtered from target, which will result in a pure titanium top surface layer (several nanometers). Although the deposition is carried out in vacuum, there is always a trace amount of oxygen in the system. The oxygen will preferably react with titanium vapor because of its higher reaction activity. The oxidization reaction adds additional weight on the titanium vapor and reduces its velocity. During the continued deposition, the velocity change will not change the Nb concentration in the body of the coating because the subsequently evaporated Nb will catch up and mix with oxidized Ti vapor, keeping the same concentration as the target. However, at the end of the deposition process, there is no additional Nb vapor to mix with the slow-moving, oxidized Ti vapor. The oxidized Ti vapor is left behind and deposited as the last layer of the coating, which leads to the Nb deficit in the coating surface layer.

Based on this hypothesis, to avoid titanium vapor oxidization in the deposition process, it is critical to eliminate the composition segregation of the coating surface layer. A modified Ti-Nb (TiNb-M) target was developed in this project to eliminate the composition segregation [5] using the sputtering deposition process.

The coating surface layer composition was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 4 shows the comparison of the XPS spectra of the coating surface layer using regular TiNb target (TiNb) and modified TiNb target (TiNb-M). It shows that the coating with the TiNb-M target has more significant Nb peaks in the spectra than that of TiNb target, which indicates that the modified target can bring Nb into the top surface layer of the coating.

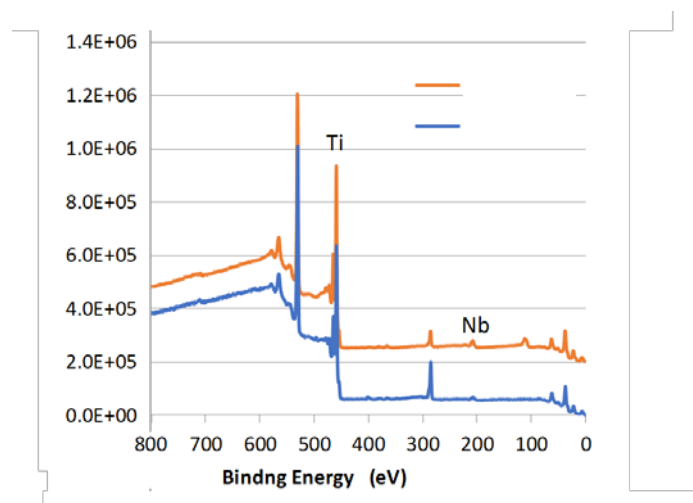


Figure 4. Comparison of XPS spectra of the as-coated SS foil with standard TiNb and modified TiNb (TiNb-M) coating, which shows that the modified target can increase Nb concentration in the Ti alloy coating surface

Conclusions and Upcoming Activities

This project is focused on the manufacturing technology development of a novel precious-metal-free coating technology for PEM fuel cell applications. A manufacturing cost analysis conducted in previous years indicates this technology will have the lowest production cost compared with other competing technologies. The project has developed technical solutions to overcome key technical barriers.

Although the project was successfully finished in February 2019, there are more challenges coming from industry.

1. Some original equipment manufacturers have more stringent ICR requirements, such as $<2 \text{ m}\Omega\cdot\text{cm}^2$ at 200 psi, which is significantly more challenging than DOE's targets.
2. While it was proven in this project that TiO_x coating has the desired low ICR and exceptional high corrosion resistance, original equipment manufacturers demand that the scientific mechanism of this coating technology be understood before they consider using this technology in their vehicles. It is necessary to conduct the fundamental investigation of the TiO_x coating for its commercial applications.
3. Use of the coating on lower-cost substrate materials, such as 304 SS, nickel-free SS, and aluminum substrate, is desired.

Further technology development should be focused in these areas.

References

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